

Area Reports

ADVANCED MATERIALS AND DEVICES RESEARCH AREA

Silicon Materials Research Task and Advanced Silicon Sheet Task

INTRODUCTION

The objectives of the Silicon Materials Task and the Advanced Silicon Sheet Task are:

- (1) To identify the critical technical barriers to low-cost silicon purification and sheet growth that must be overcome to produce a PV cell substrate material at a price consistent with FSA Project objectives.
- (2) To overcome these barriers by performing and supporting appropriate R&D.

Present solar-cell technology is based mainly on the use of silicon wafers obtained by inner-diameter slicing of Czochralski-grown ingots from Siemens reactor produced semiconductor-grade silicon. This method of producing single-crystal silicon wafers is tailored to the production of semiconductor devices rather than solar cells. The small market now offered by present solar-cell users does not justify the industrial development of high-volume silicon production techniques that would result in low-cost PV electrical energy.

It is important to develop alternative low-cost processes for producing refined silicon and sheet material suitable for long-life, high-efficiency solar PV energy conversion. To meet FSA objectives, research must be performed to overcome barriers to the successful realization of the most promising processes for producing large quantities of pure silicon and large areas of crystallized silicon at a low cost. The form of the refined silicon must be suitable for use in sheet-growth processes. The sheet, in turn, must be suitable for direct incorporation into automated industrial schemes to produce solar arrays.

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Silane can be purified relatively easily and, because of its high reactivity, can be more readily decomposed or reduced to form silicon than can trichlorosilane (TCS), the material of choice in use today in the conventional silicon production process. Thus, silicon purification involving deposition of silicon from silane is being pursued.

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Because of its potential for further reduction in the cost of silicon, research also is being conducted on a process that offers promise for making less-pure, solar-cell-grade silicon by refinement of metallurgical-grade silicon (mgSi).

Growth of crystalline silicon material in a geometry that does not require cutting to achieve proper thickness is an obvious way to eliminate costly post-production processing and material waste. Growth techniques such as EFG, dendritic-web growth (Web), low-angle silicon sheet (LASS), and edge-supported pulling (ESP) are candidates for such solar cell material. Problems generic to all sheet growth technologies are being addressed in the program. Special emphasis is placed on the dendritic web process because it seems to have the highest probability of successfully achieving the program goals for silicon sheet material.

SUMMARY OF PROGRESS

Silicon Materials Task

Semiconductor-Grade Silicon Refinement Process

Silicon Refinement Using Silane (Union Carbide Corp.)

The objective of the UCC program is to solve the critical problem of silane (SiH_4) pyrolysis in FBRs to produce semiconductor-grade silicon for PV applications. The production of ultra-pure SiH_4 by the process developed through this contract has already been demonstrated in a 100-MT/year pilot plant. The SiH_4 -to-silicon conversion reactor in this plant is a modified Siemens reactor (built by Komatsu Electrical Materials, Inc.), that does not have the potential to achieve the DOE low-cost goal for polysilicon.

The UCC program was completed on April 30, 1986. Contamination of the polysilicon product was the major problem that was addressed in this FSA Progress Report 26 period.

Early in the period, the reactor was redesigned, primarily to reduce its length to accommodate commercially available quartz-liner tubes without the need of joining two tubes to fit the original reactor length. Use of a single tube would prevent the cracking caused by misalignment of the two joined sections. The original, 110-in. length of the reactor was shortened to 84 in. Other changes included use of a stainless steel bellows to maintain sealing at the liner ends and use of a distributor plate consisting of a perforated stainless-steel plate fitted with screens in the holes. The performance of the distributor plate will approximate that of the well-qualified JPL design.

To complete the test program, three tests using quartz liners were made, ranging in duration from 54 to 72 h, and one test using a polysilicon liner, of 48-h duration. The new reactor operated well, with no liner breakage during operation. The 72-h test successfully accomplished a key contractual requirement.

In these tests, the feed concentration of SiH_4 in hydrogen was nominally in the 20 to 30% range, although higher SiH_4 concentrations up to 60%

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were tested for short durations. Operating conditions were smooth and steady, and conversion of SiH_4 to silicon was complete. Seed particles of approximately 300- μm mean diameter were grown to product particles of more than 1000- μm diameter.

Spark-source mass spectrometry as well as neutron activation were used to analyze seed and product. Excellent potential for achieving semiconductor-grade purity was demonstrated. Analytical results indicated a significant portion of the impurity content of the product is from the seed. Further work, therefore, is required in the area of high-purity seed preparation.

The final report on the contract is being prepared.

Chemical Vapor Transport Process for Purifying Metallurgical-Grade Silicon (Solar Energy Research Institute)

This program is concerned with investigation of a chemical vapor transport process in which HCl is reacted with $\text{Cu}_3\text{Si:Si}$ material (the silicon being metallurgical grade) to generate a mixture of chlorosilanes (mostly trichlorosilane). The chlorosilanes then are transported in the gaseous state and the silicon they contain is deposited by pyrolysis on a filament kept at elevated temperature, about 1050°C. The study was completed. Purification steps included:

- (1) Slagging during the electrode fabrication process to getter magnesium, calcium, barium, aluminum, manganese, and sulfur.
- (2) Selective reaction and transport because of differential diffusion rates of the elements in the alloy.
- (3) Removal of elements such as boron, titanium, molybdenum, and zirconium as chlorides by condensation on the cold walls and reactor base plate.

The maximum growth rate for deposition of the refined silicon, about 1.9 g/h, occurred for a chlorine/hydrogen ratio of 0.3 at 1100°C. The product is typically n-type with a resistivity range of 0.1 to 1 ohm-cm. It can be fabricated into cells having a 9.6% conversion efficiency without anti-reflectant coatings (baseline cells also were 9.6% efficient).

Silicon Particle Growth Research (California Institute of Technology)

The objectives of this research are to describe theoretically the growth of silicon particles from SiH_4 in a free-space reactor and to determine experimentally the conditions for maximum particle growth. This effort ended January 31, 1986.

Prior to this reporting period, the phenomenon of runaway nucleation was studied. This phenomenon involves a 10^4 -fold increase in silicon particle concentration when the SiH_4 concentration is increased from 3 to 3.4%. In the present period, experimental conditions were demonstrated that will avoid runaway nucleation. The growth of a small number of seed particles to

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supermicron size was demonstrated by controlling the rate of gas-phase reactions in a way that favored vapor diffusion to existing particles as compared to homogeneous nucleation.

Modeling of Silane Pyrolysis in Fluidized-Bed Reactors (Washington University at St. Louis)

This program is aimed at developing a model to describe the production of silicon by pyrolysis of SiH_4 in FBRs. The model will be useful for the interpretation of experimental data, for the determination of the ranges of operating parameters for maximum throughput and yield, and for providing a basis for design of scaled-up reactors for pilot plants.

The technical effort was completed and the final report published. In this program, two models were developed to treat the system in which chemical vapor deposition on silicon seed particles and gas-phase nucleation reactions to form fine particles occur simultaneously. A population balance was used to describe the size distribution of the fine particles. Growth of the seed particles was attributed to chemical vapor deposition and the capture of the fine particles on the surface of the seed particles. In the JPL FBR, good agreement was obtained between model predictions and experimental data for particle growth rate, silane conversion efficiency, and amount of fine particles formed. Effects of uncertainties in the kinetic and hydrodynamic parameters on the model predictions were discussed. Both distributor plate design and good contact between the solid phase and the silane play an important role in decreasing fine-particle formation.

Research on Pyrolysis in Fluidized-Bed Reactors (Jet Propulsion Laboratory)

The objective of this effort is to obtain a fundamental understanding of the pyrolysis of SiH_4 and the deposition of silicon in FBRs. The final report on this research was issued.

Experimental results obtained in the program indicated that more than 90% of the total silicon fed into the reactor as silane is deposited on the FBR bed particles and the remaining silicon becomes elutriated fines. The mechanism of silicon deposition from the pyrolysis of silane is described by a six-path process. Excellent purity of silicon product was obtained when a quartz liner was employed in the FBR.

Workshop

An FSA-sponsored workshop titled, "Low-Cost Polysilicon for Terrestrial Photovoltaic Solar Cell Applications," was held October 28-30, 1985, at Las Vegas, Nevada. There were more than 70 attendees, including representatives from Japan, Taiwan, Federal Republic of Germany, Canada, India, Norway, and Brazil. The workshop provided a forum for descriptions and discussions of new polysilicon processes (including those developed under FSA Project sponsorship), of polysilicon process economics, and of the polysilicon market for the semiconductor and PV industries.

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SUMMARY OF PROGRESS

Advanced Silicon Sheet Task
Shaped-Sheet Technology

Stress and Efficiency Studies in EFG Silicon (Mobil Solar Energy Corp.)

The goals of this program are:

- (1) To define low-stress configurations for silicon sheet growth that will maximize solar cell efficiency and at the same time lead to increased throughput rates.
- (2) To investigate causes of deficiency in performance of solar cells fabricated from low-resistivity silicon.

Stress analysis with increased creep rates, beyond the "high-creep" condition modeled previously, shows that significant changes in residual stress arise from the imposed transverse isotherm variations. These changes are essentially independent of the detailed shape of the transverse isotherm profile. Stress reduction is predicted only for the case where the sheet edge is cooled relative to the center.

Modeling was carried out on the influence of end effects on residual stress distributions in finite-size blanks. "Shear flow" stress distribution, used in calculation of residual stresses from laser interferometric measurements of blank curvatures under four-point bending, was obtained. Redistributed stresses were related to stress distributions in semi-infinite sheet from which the blanks were assumed to be cut.

Electron-beam-induced current (EBIC) characterization of diffusion length of float-zone silicon (that was heat treated and stressed at 1000°C) shows that larger variations in diffusion length with dislocation density are observed against background diffusion lengths. These were of the order of 100 μm than found in samples correspondingly treated at about 1200°C. A relationship between diffusion length and dislocation density was obtained for these samples.

No correlation of changes in defect density with gallium concentration levels was found in either oxygen-lean or oxygen-rich EFG material.

An apparatus was designed, constructed, and checked out to measure stress relaxation at high temperatures using four-point bending.

An extension to this contract, covering technical effort to June 30, was put into effect on April 24. The work will consist of three tasks:

- (1) Modeling studies of the effects of stress to allow correlation of theoretical results with results of experimental stress testing.
- (2) Four-point bending tests on silicon to study stress relaxation at high temperature, especially in the range of 800 to 1200°C, using the new apparatus.

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- (3) Analysis of experimental results of the stress relaxation tests to obtain an improved estimate of the creep law that can be used in modeling silicon behavior.

Dendritic-Web Ribbon Growth (Westinghouse Electric Corp.)

Westinghouse is conducting a 3-year program, which started early in CY 1984, on the development of the growth of silicon dendritic-web ribbon, and on the fabrication of high-efficiency solar cells made from this material. The purpose is to improve this dendritic-web technology and to demonstrate capabilities that are consistent with utility requirements. The CY 1985 ribbon-growth contract objectives included demonstration by mid-June of uninterruptedly, growing 2 m or more of ribbon at an area growth rate of at least $13 \text{ cm}^2/\text{min}$ under conditions of constant melt level (CML). A mid-December 1985 objective was to demonstrate an area growth rate of at least $16 \text{ cm}^2/\text{min}$ for the same conditions. The CY 1986 area growth rate objective is to demonstrate the rate required to meet DOE PV program goals, as indicated by an updated Westinghouse economic analysis.

The above CY 1985 area growth-rate objectives were not met. Improvements in this and other parameters, however, were achieved in this report period. For ribbon lengths of a meter or more, the maximum area growth rate achieved in the augmented program was increased to $10 \text{ cm}^2/\text{min}$ (for a 1.2-m-long crystal from the previous maximum of $8 \text{ cm}^2/\text{min}$). The length of the longest ribbon grown with the use of melt replenishment was increased to 17 m, for a replenishment rate between 90 and 100% of that required for constant melt level. The previous value for length of ribbon grown was 7.4 m, for a replenishment rate of only about 50%. Maximum ribbon width was increased to 6.9 cm from the previous value of 6.7 cm.

Maximum ribbon width for growth restart after a termination was increased to 6 cm from a previous value of 4.9 cm. A technique also was developed for initiating growth from "ribbon seed" (pieces of cut ribbon), and growth was initiated from such seed at a maximum width of 4.5 cm. Both of these techniques are important because their use would save considerable time required to grow ribbon to wide widths (typical widening rates are around 1 cm/h).

A record was set for throughput (defined as ribbon area grown in a single furnace in a week's time, 7 days) for replenished growth. The throughput was raised to $47,000 \text{ cm}^2$ from its previous record value of $27,000 \text{ cm}^2$.

Considerable progress was made toward automated closed-loop control of the ribbon growth process. In July 1985, the first demonstrations of closed-loop furnace-temperature control were successfully made. The control system employed the dendrite thickness monitor, which performs simultaneous, non-contact sensing of the thicknesses of the two dendrites of a growing crystal and compares these thicknesses with a reference value. In one 5-h test, a ribbon of 5.5 m length was grown without operator intervention. The test was terminated intentionally for manual melt replenishment. In these initial tests, with the heater coil being stationary, the average dendrite thickness

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was controlled. In the November/December period, simultaneous operations were accomplished for both the closed-loop melt replenishment and temperature control systems, and the closed-loop heater coil position and temperature control systems under conditions of constant melt level (achieved by manual replenishment). The control system for heater coil position allows control of the thickness of both dendrites to the proper values, rather than control of the average thickness. The maximum period for continuous growth under conditions of closed-loop control of heater coil position and melt temperature for constant melt level was 5.5 h. More than 60 h of accumulated run time were conducted with various combinations of closed-loop control functions.

Refinement of the thermal stress model permitted calculations of the temperature and stress distributions in ribbon from the melting point (growth interface) to room temperature. Elastic buckling studies indicate that interface stresses and those caused by final cooldown do not currently limit area growth rate. Application of a Penning-Jordan-type plastic flow analysis produced good agreement between calculated residual stresses and those measured on actual ribbons. New lower-stress designs based on these analyses gave improved ribbon growth, including the record width of 6.9 cm.

An extension of the contract to Westinghouse, covering the calendar year (CY) 1986 effort on development of the ribbon growth process, was put into effect on February 21, 1986.

Silicon Sheet Supporting Studies

Modification of Silicon Surface Properties by Fluid Absorption (University of Illinois at Chicago)

In this program, the modification of silicon surface properties by various fluids is being studied, and residual stress in silicon sheet is being measured by laser interferometry.

High-temperature indentation damage in silicon was evaluated by using a recently completed high-temperature indentation fixture. Radial crack length, as a function of indentation temperature, was measured over the range from 25 to 300°C. Indentations were made in (100) p-type and (100) n-type Cz silicon. The data indicate that crack length remains constant from 100 to 250°C. This plateau is expected to have a significant influence on sawing, since elevated temperatures are expected because of the sliding contact. The data also indicate that the crack lengths for p-type silicon typically are smaller than for n-type silicon.

A high-speed, high-temperature cutting facility was constructed to cut silicon at a precise feed rate, depth of cut, and fluid environment. The surface morphology and debris size analysis are being used to indicate the deformation mode. For cuts made in air, the average debris size decreases from 1.7 to 1.0 μm when the temperature is raised from room temperature to 100°C. At room temperature, the average debris size increases from 1.7 to 5.6 μm for cuts made in air and ethanol, respectively. The surface morphology of the groove also varies with fluid and temperature. For deionized water and ethanol, as temperature is increased from room temperature to 100°C, the ploughed regions broaden by a factor of two.

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The damage formed during scratching and/or indentation was modeled by dislocations propagating in the space charge field of the silicon. The surface of the silicon was described by a limited number of surface sites that may interact with fluids or adsorbates. Because surface sites are limited, they may not sustain the surface charge necessary for equilibrium, and the extent of the space charge region may vary with the surface site density and energy as well as the electrochemical potential.

The Debye length that may be calculated by this model is therefore related to the damage zone (generated by indentation), since dislocations must propagate in the space charge field.

Efforts continued on measuring residual stress in silicon sheet materials using shadow moiré and laser interferometry. Residual stress distributions were determined for EFG and dendritic web ribbon samples. The results consistently indicated that for both sheet materials, the edges of the sheet are in compression while the center region is in tension. The EFG samples have a consistently higher residual stress of 5 to 10 MPa as compared with the dendritic web material stress of 0.5 MPa.

Analysis of Stress/Strain Relationships (University of Kentucky)

This program is aimed at developing stress/strain models for silicon sheet growth processes and evaluating the relationship between silicon growth structure and stress/strain.

Significant progress was made in the following areas:

- (1) Elevated-temperature tensile tests on Cz and dendritic web ribbon material.
- (2) Dislocation mapping, including preferred slip orientations, dislocation mobility, and dislocation multiplication.
- (3) Stress/strain analysis, through use of the Sumino-Haasen dislocation model.

Several tensile tests of Cz silicon samples were conducted at 800 to 1000°C. The data are close to those obtained by K. Sumino. Elevated-temperature tensile testing has been difficult. Some furnace sealing problems were solved, and now a vacuum of 10^{-6} torr can be achieved. Molybdenum test grips are used in a 1% hydrogen-in-argon gas mixture. Specimens tested have had several crystallographic orientations, and different slip systems can be identified after the test is complete. Stress/strain curves were produced. Preliminary initial yield data (strain rate of 4×10^{-4} to $13 \times 10^{-4} \text{ s}^{-1}$) for 800, 900, and 1000°C are approximately 29, 20, and 10 MPa, respectively.

Successful tensile tests on Westinghouse web samples were carried out at 1100 and 1150°C. Reproducibility of test results at 1100°C and 10^{-4} s^{-1} strain rate seemed very good. Flow stress values are comparable with Cz data. Cz samples were used to study effects of laser-cut edges. Significant differences in stress/strain behavior were noted for polished versus unpolished edges.

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Studies began on the behavior of a single dislocation moving in the stress field associated with a Westinghouse ribbon thermal profile. This activity complements both University of Kentucky continuum calculations and Westinghouse's activity. These studies involve 3-cm-wide ribbon with only half the ribbon considered. Dislocations introduced at two different positions on the growth interface both end up at the ribbon centerline. Calculations were made using single-dislocation considerations (no interactions of any kind) and only motion in glide was considered.

In the area of dislocation mapping, dislocations are "inserted" analytically at the ribbon melt interface at various positions across the ribbon width. Subsequent motion of each dislocation is tracked as it moves through the thermal stress field. Evaluation of analytical results to date indicates significant dislocation motion and multiplication occur within the first 0.5 cm of the 3-cm-wide ribbon melt interface.

Efforts are just beginning in the area of experimental microstructural observations correlated with stress/buckling phenomena.

In the stress/strain activity, analyses were carried out of thermal stresses associated with a Westinghouse temperature profile, $T(x) = 1292 + 120e^{-5x} - 86.5x$. Most of the large growth stresses are near the growth interface for this profile. The final dislocation value is $3 \times 10^3/\text{cm}^2$ near the center, and $1.1 \times 10^3/\text{cm}^2$ near the outside edge. The first five buckling modes also were predicted and graphically documented. A critical buckling thickness of 158 μm was calculated for a 6 x 12 cm piece of ribbon.

Residual stresses, developed in a ribbon grown with a newer temperature profile, $T(x) = 1372 + 40e^{-5x} - 99.83x$, were calculated. Low residual stress values were obtained that were relatively consistent with Westinghouse splitwidth residual stress measurements. During this period, the maximum (critical) width to which ribbon could be grown in the Westinghouse thermal profile (given above in this paragraph) also was calculated with zero starting dislocation ($N_0 = 0$). A critical width is predicted of above 6 cm. As the starting dislocation density increases, the critical width decreases. For example, for $N_0 = 30/\text{cm}^2$ the critical width is predicted to be about 3.5 cm.

Based on work performed in this program, a paper titled, "Thermal Stresses and Buckling of Elastic Plates with Reinforced Edges," was presented at the Southeastern Conference on Theoretical Applied Mechanics held in Columbia, North Carolina, in April 1986.

Analysis of High-Speed Growth of Silicon Sheets in Inclined-Meniscus Configurations (Massachusetts Institute of Technology)

Work continued to identify the parameters and operating conditions for high-speed growth of thin silicon sheet. The thermal-capillary model and finite-element analysis were used to describe the growth of thin silicon sheets both with planar and with deformed melt-solid interfaces. Dependence of crystal thickness upon pull speed was computed, and the thickness was found to decrease with increasing pull speed. Because the inclined meniscus further

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reduces the thickness, it consequently limits the pull speed. The melt-solid interface remained flat with a deflection of 6 to 7% over the range of pull speeds. The higher melt-solid interface deflection encountered with dendritic web ribbon growth cannot be explained by low-axial temperature gradient.

Because of the roll-off in Project funding, the contract to the Massachusetts Institute of Technology is being terminated.

Optimization of Silicon Crystals for High-Efficiency Solar Cells (Solar Energy Research Institute)

This program was completed on March 31, 1986. Silicon crystal growth parameter effects on minority-carrier lifetime were investigated using high-purity FZ techniques. The goals of the work were:

- (1) To optimize dopants and minority carrier lifetime in FZ material for high-efficiency solar cell applications.
- (2) To improve understanding of life-time degradation mechanisms (point defects, impurities, thermal history, etc.).
- (3) To characterize lifetime-related crystallographic defects in silicon crystals by x-ray topography.

Float zoning of high-purity, dislocation-free silicon was conducted both as a tool to study minority-carrier lifetime dependence on various growth parameters, and also as a means of growing long-lifetime, heavily-doped, p-type silicon for use in solar cells. Lifetime values of 303 μ s for 0.46 ohm-cm resistivity silicon and 214 μ s for 0.36 ohm-cm resistivity silicon were achieved when gallium was used as the p-type dopant in [100] crystals. Dislocation-free crystals doped with boron, aluminum, indium, and gallium over a range of resistivities also were grown to establish correlations between lifetime and resistivity with dopant species as a parameter. The effect of crystal cooling rate on lifetime was determined in the range 50 to 600°C/min. The lifetime decreased with increasing cooling rate for both dislocation-free and dislocated crystals. The presence of dislocations, however, had a much more dominant effect in degrading lifetime than did cooling rate.

Calculation techniques and pertinent property data were developed for a comparison of vacuum and gas ambients as they affect impurity concentration profiles in float-zoned and cold-crucible-grown crystals. Graphical impurity profiles were obtained for various segregation and evaporation coefficients in the general case and also for the specific impurities in silicon of aluminum, antimony, arsenic, boron, copper, gallium, gold, indium, iron, manganese, and phosphorus. Results indicated that multiple pre-passes in vacuum prior to the crystal growth pass were helpful in reducing the content of most metallic impurities to negligible levels.

X-ray topography was used to examine both dislocations and lattice-plane curvature in silicon ribbons grown by various methods, and to look at micro-defects in dislocation-free silicon crystals. Improvements also were made in lifetime measurement of heavily-doped silicon.

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The draft final report on this program was written and reviewed by cognizant JPL personnel. The final report is being published.

Crystal Growth Modeling Studies (Washington University at St. Louis)

The purpose of this study is to develop a mathematical model describing the Cz crystal growth process. The model is intended to serve as a basis for predicting the important process parameters such as pulling rate and interface shape, to provide strategies for growth of large-diameter crystals, and to lead to improved process control algorithms.

A conduction-dominated model was developed, suitable for predicting the temperature distribution in the crystal and for calculating the melt-crystal interface shape for an assumed melt temperature profile and heat transfer coefficient. A simple model then was developed that correlates the pulling rate and the interface shape as a function of major operating parameters, such as crystal radius and crucible temperature. This simple model correctly portrays the more detailed conduction-dominated model and is therefore suitable for computer control of the growth process.

An analytical study was made of the use of a cooling jet of argon to control the crystallization in the Cz process. This would increase the ingot growth rate and to improve the crystal quality. The effect of jet cooling on the interface shape and pulling rate is significant, and the crystal diameter tends to be more stable in the rapid-cooling environment of the jet.

A study was performed of stress effects for Cz growth. Stresses can be calculated by finite-element analysis, and the effect of growth interface shape on stresses was determined.

Because of the roll-off in Project funding, the contract to Washington University at St. Louis is being terminated. As a result, a stress study to determine the effects of localized high-thermal gradients induced by jet cooling will not be completed.

Electrical, Structural, and Chemical Characterization of Silicon Sheet Material (Cornell University)

The objective of this program is to investigate the physical structure and the chemical nature of defects in silicon sheet material.

The high-temperature deformation of silicon dendritic web ribbon is being studied to obtain accurate creep data for modeling stress relaxation in this silicon material.

Four-point bending at 1000°C was carried out at Mobil Solar Energy Corp. Testing revealed a unique two-stage deformation behavior for dendritic web ribbon that is very different from either single-crystal silicon (either FZ or Cz) or from polycrystalline material (such as EFG silicon). A dendritic web sample subjected to a load initially showed a high creep rate, but after about 1 min the creep rate decreased to almost zero. Then, another period of rapid creep commenced, followed by a period of slow creep. This sequence repeated

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itself one more time before the test was ended and confirmed results that had been obtained previously by Cornell. Two samples from the same ribbon, loaded under identical conditions, showed strain bursts at the identical strains, indicating that this behavior is related to crystal morphology and conceivably linked to the presence of two planes in the ribbon.

Preliminary analysis of the data obtained at 1000°C by four-point bending of dendritic web ribbons yielded a value for creep strain rate, $\dot{\epsilon}$, of $8.81 \times 10^{-8} \sigma^3 \text{ s}^{-1}$, where σ is the stress in MPa. This result is in good agreement with the data measured for Cz and dendritic web materials by the University of Kentucky.

Oxygen measurements by Fourier transform infrared (FTIR) spectroscopy reveal a very high oxygen content of about 20 ppma (near the solubility limit) for dendritic web silicon. In addition, a shoulder on the 9- μm infrared (IR) absorption peak of interstitial oxygen in silicon in many of the samples has been variously linked to SiO_2 in the form of coesite at the cores of dislocations, and to complexes of silicon, O, and vacancies absorbing in this IR region. Appearance or lack of this shoulder has not been correlated to the growth configuration, or any other known sample parameter.

Width of the absorption peak associated with interstitial oxygen in silicon is wider in the dendritic web silicon (about 35 to 45 cm^{-1}) than in Cz silicon (about 33 cm^{-1}). A wider absorption peak is generally thought to be related to stress in the specimen, but no quantitative analysis of this effect has been carried out. In two samples with a known amount of stress, the sample with the higher stress had a wider absorption peak than the sample with the lower stress.

Width of the IR absorption peak decreased by annealing a high-stress sample at 850°C for 24 h. This phenomenon was not observed with a low-stress sample.

Materials Properties Modification (Jet Propulsion Laboratory)

Effort was focused on developing a constitutive equation for the behavior of silicon deformation at high temperatures and to obtain improved model predictions for stable ribbon growth. A large variation exists in the constitutive equations and parameters used by different investigators to describe plastic deformation and buckling of ribbon at high temperature. Consequently, correlation of their results is difficult. For example, using results from Mobil Solar Energy's experiments on high-temperature creep response of several Cz and FZ silicon samples by four-point bending, an attempt was made to evaluate the creep data by using equations for primary and secondary creep. The results, however, indicated no correlation between the Mobil-based data and published information.

Several important equations were discussed and evaluated in the FSA-sponsored stress/strain workshop held at the University of Kentucky on March 18-19, 1986. An equation used by most investigators, including K. Sumino of Japan, is recommended as a standard constitutive equation for high-temperature deformation of single-crystal silicon. Values from the literature for the parameters in this constitutive equation were compiled. Efforts continue to define and refine the constitutive equation.

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In the effort on measurement of high-temperature properties of silicon sheet, Cz tensile samples tested at 1000°C to 4% total strain were characterized by x-ray transmission topography. Several microstructural features were noted:

- (1) Extensive structure was generated in a nonhomogeneous manner throughout the reduced-gage section of the sample.
- (2) Structure was generated from stress concentration sites at both the extensometer pinholes and the loading pinholes.
- (3) Greater plastic deformation around sample holes were observed for [220] topographs than for [422] topographs.

Because of these problems, a new test sample configuration and processing procedures were developed. Ultrasonic machining of the test samples of either Cz or dendritic web material is now possible as compared to the previously used microgrit blasting technique. With appropriate protective coatings on the silicon sheet faces, the as-cut samples are planar-etched only on the edges to remove damage induced by the ultrasonic cutting. All sample configuration tolerances have been significantly tightened. In addition, the ratio of tab to active gage cross-sectional area has been increased from 2:1 to 5:1 for old versus new sample designs.

The testing equipment, used for tensile tests, is being calibrated after addition of a high-vacuum capability to the elevated-temperature furnace

A systematic study was conducted involving measuring the structural and electrical characteristics of low- and high-stress Westinghouse dendritic web ribbon as a function of annealing temperature in the range of 450 to 1050°C. The lower-stress ribbon had residual stresses ranging from 1.0 to 9.5 Mdyn/cm² while the residual stresses for the higher-stress material were measured to be between 38 and 40 Mdyn/cm². Results indicate the minority carrier lifetime of web ribbon can be improved with annealing. Magnitude of improvement in the lifetime depends on annealing temperature and residual stress of the material. Material with lower residual stress improved by an order of magnitude, while the higher-stress material improved by a factor of six. The peak in the lifetime improvement for the higher stress material occurred at a lower annealing temperature than for low-stress ribbon. In both cases, the peak lifetime was at a temperature lower than the usual processing temperature for n⁺-p junction formation. This implies that devices should be processed at a temperature lower than the one standardly used, to optimize fully the performance of solar cells.

Workshop

A workshop at the University of Kentucky, Lexington, Kentucky on March 18 and 19 was organized and sponsored by the FSA Advanced Silicon Sheet Task to review progress relating to control of stress and strain during silicon ribbon growth. About 20 people attended including contractors, JPL participants, and other PV program representatives.

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The presented results indicated considerable progress in understanding the stress and strain problem from both an analytical and experimental approach. Specifically, several technical conclusions were reached. The use of elastic approximations is appropriate in that strains are small (except for calculations of residual stress). Mechanical property measurements will be confined to the low-strain regime (a very difficult region in which to make measurements). Calculations of ribbon-dislocation distribution qualitatively agree with experimental observation. Observed dislocation densities are generally lower than calculated. Critical maximum values of ribbon width and pull speed may exist that are only slightly greater than those presently being achieved.